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(54) Title: PLATINUM-FREE ELECTROCATALYST MATERIALS

(57) Abstract: New metal-based catalyst materials, non-containing platinum, for preferred application to form both alcohol-tolerant cathodes for oxygen reduction and anodes for oxidation of various fuel molecules, and methods of making the said catalysts are provided. Methods for preparing anodes and cathodes for fuel cells are also provided.

## PLATINUM-FREE ELECTROCATALYST MATERIALS

### Field of the invention

The present invention pertains in general to supported catalysts based on transition metals, other than platinum, and to their use in fuel cells, which are 5 suitable for a variety of uses such as anodes and cathodes in fuel cells, as reformer catalysts, as oxidation catalysts, as water-gas shift catalysts, in metal-air batteries, as oxygen sensors and oxygen recombination catalysts. In particular, this invention relates to catalysts specifically designed for application as either 10 alcohol-tolerant cathode materials for catalytic oxygen reduction or anode materials for catalytic oxidation of fuel molecules.

### State of the art

Fuel cells are electrochemical devices that convert the chemical energy of a reaction directly into electrical power. In such cells, a fuel (generally hydrogen, alcohols or saturated hydrocarbons) and an oxidant (generally oxygen from air) 15 are fed in a continuous supply to the electrodes. Theoretically, a fuel cell can produce electrical energy for as long as the fuel and oxidant are supplied to the electrodes. In reality, degradation or malfunction of the components limits the practical operating life of fuel cells.

A variety of fuel cells are in different stages of development; considering, in 20 particular, fuel cells in which electrocatalysts of the type described and claimed in the present invention can be used, the following can be mentioned as examples: Polymer Electrolyte Fuel cells (PEFC) fuelled with H<sub>2</sub>, Direct Oxidation Fuel Cells (DOFC) fuelled with alcohols (Direct Alcohol Fuel Cell, DAFC) or with any other hydrogen-containing liquid or gaseous fuel (alcohols, glycols, aldehydes, saturated 25 hydrocarbons, carboxylic acids, etc), Phosphoric Acids Fuel Cells (PAFC) and Molten Carbonate Fuel Cells (MCFC).

Essential components of any fuel cell of the types mentioned above are the electrodes that in general contain metals or metal particles supported on porous carbon materials bound to a suitable conductor. Catalysts usually employed for 30 reducing the oxygen comprise transition metals, such as platinum, nickel, cobalt, silver, to mention but a few. Catalysts usually employed for oxidizing the fuel (for example H<sub>2</sub> in the PEFCs and methanol in the Direct Methanol Fuel Cells (DMFC)

are platinum, platinum-ruthenium, platinum-ruthenium-molybdenum and platinum-tin mixtures. All the fuel cells producing an acceptable cell potential ( $> 0.5$  V) contain platinum, alone or in conjunction with other metals, preferably ruthenium, at the anode, while the cathode is generally formed by platinum, yet other metals 5 can be equally employed. The preferred presence of platinum, generally in high loadings, represents a major economic limitation to the mass production of fuel cells for transportation, cellular phones and electronic devices in general. Indeed, the high cost of platinum (currently, around 25-30 USD/g) contributes to make the cost of power produced by a fuel cell much greater than the cost of other power 10 generation alternatives. Moreover, platinum-based cathodes in DMFC's are sensitive to cross-over methanol. Given the higher efficiency of fuel cells as compared to traditional power generation methods as well as their environmentally benign nature, it is highly desirable to develop fuel cells that do not require platinum.

15 To the best of the applicant's knowledge, platinum is an essential component in the anodes for the DOFCs or PEFCs available at present.

US-A-4828941 describes methanol/air fuel cells where the cathode contains as the catalytic component, a Co(salen) compound or a polymer containing this compound. It is not possible to dispense with platinum as a catalyst for the 20 oxidation of methanol in the claimed electrochemical cell.

In US-A-6245707 is illustrated the synthesis of methanol-tolerant cathodes for oxygen reduction, obtained by mixing together and heat-treating at least two different transition metal-containing nitrogen chelates. The nitrogen chelates comprise metalloporphyrins and preferred transition metals are iron, cobalt, nickel, 25 copper, manganese, ruthenium, vanadium and zinc.

Catalysed cathodes for fuel cells, comprising a mixture of cobalt acetate and polyacrilonitrile are described in US-A-5358803.

US-A-5240893 describes a method of preparing electrodes, in particular cathodes, formed with pyrolysed metal-heterocarbon-nitrogen material where the metal is 30 cobalt, nickel, iron, copper, vanadium, chromium, and manganese and mixtures thereof. A polymer is obtained by reacting an amine compound with formaldehyde or polymerised formaldehyde in the presence of an alkali catalyst. The polymer,

isolated or formed in situ, is reacted with carbon particles and a metal salt to give a polymerised product in the form of a gel, which is baked at 800 °C for 1 h. The resulting powder is mixed with a binder and used to make electrodes. Irrespective of the metal dopant, the specific power supplied by these cathodes consists of a few tens of mW/cm<sup>2</sup> at low current density.

5 DE-A-2549083 reports the preparation of platinum-free cathodes for fuel cells, based on iron phthalocyanines.

10 WO-A-0196264 describes Fischer-Tropsch catalysts constituted by a matrix comprising a polymer, generally polyacrylate or polymetacrylate, and at least two metals, one of which being iron, cobalt, nickel and chromium, the other metal being iron, silver, zinc, platinum, zirconium, or mixtures thereof.

#### Descriptions of the drawings

Fig. 1 represents a cross-section schematic view of a simplified fuel cell operating with the catalyst of the invention.

15 Fig. 2 reports the anodic polarization curves for the different materials in 2N H<sub>2</sub>SO<sub>4</sub> – 1N CH<sub>3</sub>OH solution saturated with air.

Fig. 3 shows the cathodic polarization curves for the different materials in 2N H<sub>2</sub>SO<sub>4</sub> – 1N CH<sub>3</sub>OH solution saturated with air.

20 Fig. 4 shows the anodic polarization curves for the different materials in 1N KOH – 1N CH<sub>3</sub>OH solution saturated with air.

Fig. 5 shows the cathodic polarization curves for the different materials in 1N KOH – 1N CH<sub>3</sub>OH solution saturated with air.

Fig. 6 shows the change with time of the performance of a DMFC using the electrodes made with catalysts the invention.

25 Fig. 7 shows in a flow diagram the various process steps from the starting reagents for preparing the polymer down to the metal-doped catalytic materials used for producing the electrodes.

#### Detailed description of the invention

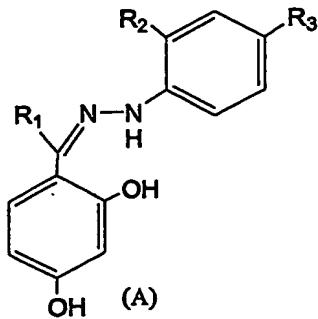
The Applicant has now found that new templating polymers, formed by 30 condensation of a 4-{1-[(2,4-di(substituted)-phenyl)-hydrazone]-alkyl}-benzene-1,3-diol with a 3,5-disubstituted phenol and formaldehyde or paraformaldehyde, coordinate transition metal salts, yielding, after treatment with appropriate reducing

agents and immobilization on support materials (porous carbons, graphite, metallic powders, etc), very efficient catalysts for electrochemical cells, for example capable of producing powers at ambient temperature and pressure as high as 160 mW/cm<sup>2</sup>, when directly fuelled with methanol, and as high as 300 mW/cm<sup>2</sup> when fuelled with H<sub>2</sub>.

In a first embodiment the present invention refers therefore to nitrogen-oxygen-carbon polymers (hereinafter indicated with P) suitable for the coordination of metal salts other than platinum salts.

According to the invention with nitrogen-oxygen-carbon polymers are intended polymers obtained by condensation of a 4-{1-[(2,4-di(substituted)-phenyl)-hydrazono]-alkyl}-benzene-1,3-diol with a 3,5-disubstituted phenol and formaldehyde or paraformaldehyde in the presence of either a basic (e. g. NaOH) or acid (e. g. HCl) catalyst in water/alcohol mixtures as solvent and at a temperature sufficient to form a methylol intermediate compound (according to Scheme I).

For 4-{1-[(2,4-di(substituted)-phenyl)-hydrazono]-alkyl}-benzene-1,3-diol, according to the invention is intended a compound of formula (A):

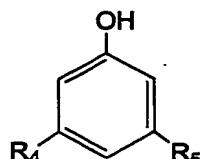


wherein R<sub>1</sub> is chosen in the group consisting of: hydrogen and a hydrocarbon radical, preferably aliphatic, having from 1 to 10 carbon atoms, possibly halogenated, more preferentially methyl or ethyl.

R<sub>2</sub> and R<sub>3</sub> each independently represent a preferentially electron-withdrawing group selected in the group consisting of hydrogen, halogen, acyl, ester, carboxylic acid, formyl, nitrile, sulphonic acid, linear or branched alkyl or aryl groups, having from 1 to 15 carbon atoms, optionally functionalised with halogens or joined to each other to form one or more condensed cycles with the phenyl ring,

and nitro groups.

For 3,5-disubstituted phenol according to the invention is intended a compound of formula (B):



5 (B)

wherein R<sub>4</sub> and R<sub>5</sub> each independently represent an electron-donating group selected in the group consisting of hydrogen, hydroxyl, ether, amines, aryl and linear and branched alkyl groups, having from 1 to 15 carbon atoms.

10 According to the invention acyl means a group COR' wherein R' is preferably a C<sub>1-10</sub> alkyl or aryl, ester means a group COOR' wherein R' is as above defined, ether means a group OR' wherein R' is as above defined, amines means a group NR"R'" wherein R" and R'" same or different from each other are H, C<sub>1-10</sub> alkyl, aryl; in all the above reported definitions aryl means preferably phenyl, naphtyl and

15 higher homologues.

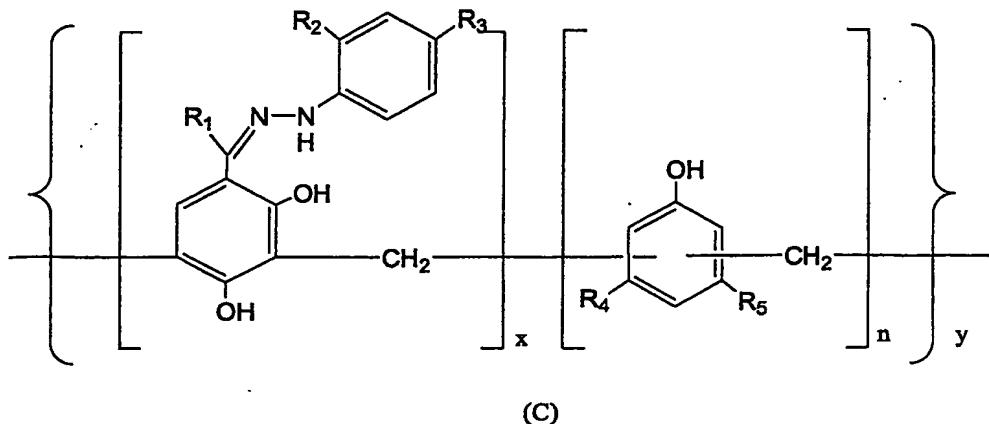
Between formaldehyde and paraformaldehyde the second is preferred.

The nitrogen-oxygen-carbon polymers P are obtained, see hereinafter, as brick red solids generally soluble in polar organic solvents, such as dimethylsulfoxide, dimethylformamide, 1,4-dioxane, acetone, tetrahydrofuran.

20 The most likely structure of P is similar to that of a phenolic resin (Bakelite) with phenol units replaced by 4-{1-[(2,4-di(substituted)-phenyl)-hydrazono]-alkyl}-benzene-1,3-diol units that contribute to modulate the chemical-physical properties of the polymer itself. As the two phenol derivatives (A) and (B) can both react with formaldehyde to produce a macromolecular structure, further modulation of P can

25 be achieved by varying their initial molar ratio (A/B); preferably, according to the invention, such initial molar ratio a/b is comprised between 0.5 and 2, more preferably is 0.7.

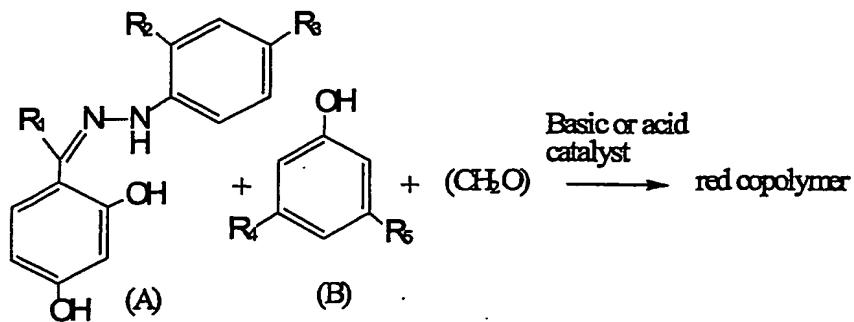
The polymer according to the invention can also be represented by the following formula (C):



wherein y can vary from 2 to 120, x can vary between 1 and 2, n can vary between 1 and 3 and R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> and R<sub>5</sub> are as above defined.

5 As one in the art can realize looking at the above reported formula, the polymer P according to the invention has available both nitrogen and oxygen atoms for binding metal centres, preferentially in chelating fashion. IR and NMR spectra of P show unequivocally the presence of both NH and OH groups. The P materials can be dried at 150 °C for some hours in the air with no decomposition. Average 10 number molecular weights can be modulated in a broad range, between about 1000 and about 50000, by properly varying the experimental conditions.

According to a preferred method of production the polymers P of the invention are obtained by condensation of a 4-{1-[(2,4-di(substituted)-phenyl)-hydrazone]-alkyl}-15 benzene-1,3-diol with a 3,5-disubstituted phenol and formaldehyde or paraformaldehyde in the presence of either a basic (e. g. NaOH) or acid (e. g. HCl) catalyst in water/alcohol mixtures as solvent at a temperature sufficient to form a methylol intermediate compound (according to the following Scheme I):



Scheme I

wherein:  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$  and  $R_5$  are as above defined.

The 4-{1-[(2,4-di(substituted)-phenyl)-hydrazono]-alkyl}-benzene-1,3-diol reagents are synthesized via condensation of appropriate 4-acyl/formyl-benzene-1,3-diols with 2,4-disubstituted phenylhydrazines.

The polymers P are also obtained by a one-pot or cascade procedure using as separated components 4-acyl/formyl-benzene-1,3-diol, 2,4-disubstituted phenylhydrazine, 3,5-disubstituted phenols and formaldehyde or paraformaldehyde with the substituents mentioned above.

Preferably the reaction temperature is comprised between about 20 to about 150 °C and the pH ranges from about 1 to about 14.

According to a second embodiment the present invention refers to a complex consisting of a polymer as above described and a metal salt.

In fact the excellent ligating properties of P allow the stable complexation of a large variety of metal salts preferably transition metals salts and, more preferably iron-, cobalt- and nickel-carboxylates, -halides, -alcoholates, -acetylacetones, -formates, -oxalates, -malonates, and analogous organic salts and mixtures thereof.

Inorganic salts such as carbonates, oxides and bicarbonates, etc., and mixtures thereof, are also suitable for the purpose provided they are capable, according to what is known in inorganic chemistry, of interacting with the polymer P in the reaction environment in order to form a coordination complex.

Fe-, Co- and Ni-acetates (and mixture thereof) are particularly preferred.

The complexes according to the invention can be obtained by stirring a suspension of P with a metal salt or a mixture of metal salts, more preferentially nickel(II), iron(II) and cobalt(II) salts, dissolved preferentially in water or water/alcohol. The reaction produces a material where the metal salt(s) is (are) strongly tethered to P and maintain the oxidation state of the molecular precursors.

The metal-doped materials obtained, hereafter denoted as P-M (M = main group or transition metal) are very stable: they can be washed several times with boiling water without losing the anchored metal salt(s).

Following the preferred procedure described above, the overall metal

concentration in the said metal-doped materials P-M can be appropriately varied in the range 0.5-10 wt. %.

Notably, the reaction of P with two metal salts in a desired ratio or the reaction of P with n metal salts in desired ratios gives P-M materials where the original ratio of

5 the added metals is fully maintained. Therefore, the reaction of P with, for example,  $\text{Fe}(\text{OAc})_2$ ,  $\text{Ni}(\text{OAc})_2$  and  $\text{Co}(\text{OAc})_2$  ( $\text{OAc}$  = acetate) in a 1:1:1 stoichiometric ratio will give a P-M material containing iron(II), nickel(II) and cobalt(II) ions in a 1:1:1 molar ratio.

According to a further embodiment, the present application refers to catalysts 10 obtained from the above described P-M materials and to electrodes for fuel cells comprising such catalysts in conjunction with a suitable conductive support. Moreover the invention refers also to fuel cells comprising the electrodes according to the invention.

The catalysts of this invention contain metals, other than platinum, more 15 preferentially nickel, cobalt, iron and mixtures thereof and are unexpectedly capable of catalysing the reduction of oxygen as well as the oxidation of various gaseous and liquid substrates ( $\text{H}_2$ , methanol, ethylene glycol and higher glycols, gasoline, formaldehyde, hydrazine to say but a few). The applicant has also found that these catalysts form efficient electrodes for different types of fuel cells. In 20 particular, the applicant has surprisingly found that the anode requires the presence of nickel, alone or in binary and ternary combinations with cobalt and iron, whereas, in a preferred method, the cathode contains nickel or cobalt alone. Moreover, the cathodes of the invention are fully tolerant to cross-over alcohols, which allows the use of higher alcohol concentrations (up to 50% in volume) than 25 in platinum-based DAFC's.

In order to produce the catalysts of the invention, the P-M materials are treated with reducing agents either in the solid state with  $\text{H}_2$  or in fluid solution systems. Therefore, a solid sample of the P-M material is dispersed in a solvent, preferentially water/alcohol mixtures and then treated with a solution of a reducing 30 agent, preferentially an aqueous solution of hydrazine, more preferentially a solution of a tetrahydroborate salt  $[\text{Y}] \text{BH}_4$  at a temperature between  $-10$  °C and 30 °C, wherein Y is an alkali metal cation, such as  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , or an organic cation

such as tetraalkylammonium  $(NR_4)^+$ , and bis(triphenylphosphoranylidene)ammonium  $(PPN^+)$ , just to say but a few.

According to another process for producing the catalysts of the invention, a solid sample of the P-M material is baked at an appropriate temperature between 500 5 and 1000 °C, preferentially 800 °C, under inert gas protection (for example  $N_2$ , Ar) for about 2 hours.

In a preferred method for making the catalysts of the invention, especially to form anodes for fuel cells as exemplified schematically in Figure 1, the P-M materials are preliminary supported on either a porous carbon support material (Vulkan XC-10 72, active carbon RBDA, standard R-5000, NSM-III, Ketjen black and Raven-1020, graphite, etc.) or other conductive support materials such as finely powdered silver, nickel and others, prior to treatment with reducing agents either in the solid state or in fluid solution systems. The reduction of the metal centres occurs with formation of heterocarbon-supported metal particles (HC-P-M) where M is 15 constituted by a single metal or a mixture of metals other than platinum.

In another preferred method for making anodes for fuel cells, solid P-M materials are treated with a flow of  $H_2$  at about 350-400 °C for about 1-2 hours.

Due to the excellent affinity of P for metal salts, the said heterocarbon-supported catalysts HC-P-M can also be prepared in a one-pot or cascade procedure by 20 mixing P, a metal salt or more than one salt of different metals, and the carbon support in an appropriate solvent and the resulting mixture is treated with a reducing agent such as hydrazine or a tetrahydroborate salt, just to say but a few. In a preferred method for making the catalysts of the invention HC-P-M, especially to form cathodes for fuel cells, the P-M materials are preliminary supported on 25 either a porous carbon support material (Vulkan XC-72, active carbon RBDA, standard R-5000, NSM-III, Ketjen black and Raven-1020, graphite, etc.) or other conductive support materials such as finely powdered silver, nickel and others, prior to heat-treatment at an appropriate temperature between 500 °C and 1000 °C, preferentially 800 °C, under inert gas protection (for example  $N_2$ , Ar) for about 30 2 hours.

A general procedure for preparing both anodes and cathodes from the catalysts of the invention is as follows:

A portion of HC-P-M is suspended in a 1:1 mixture of water/alcohol with vigorous stirring at room temperature. To this suspension is added with stirring non-wetting agent, such as polytetrafluoroethylene (PTFE) (60 wt % dispersion in water, Aldrich) (ca. 20 wt % with respect to HC-P-M). Vigorous stirring is maintained for ca. 10 min to give a flocculate material. The reaction vessel is sonicated until a rubber-like material is formed, which is separated by decantation. This material is rolled on either carbon paper, sintered graphite, or metallic nets (steel, nickel, etc), and pressed at about 100 Kg/cm<sup>2</sup>. The electrode so formed is baked at 350-400 °C under an inert atmosphere (N<sub>2</sub>, Ar).

The present invention is further described by the following examples, which, however, are provided for purely illustrative purposes and do not limit the overall scope of the invention itself.

Three preferred procedures for making the polymer P are described in Examples 1, 2 and 3.

**EXAMPLE 1**

To a suspension of 32 g of finely dispersed 4-{1-[(2,4-dinitrophenyl)-hydrazono]-ethyl}-benzene-1,3-diol in 200 mL of water is added 10 g of phenol and 10 mL of aqueous formaldehyde (40 wt. %) at room temperature. To this mixture is added solid NaOH (0.5 g) with stirring. The resulting dark brown suspension is refluxed four 8 hours at 110 °C to give a dark brown solid. The solid is filtered, washed several times with cold water and then added to 500 mL of distilled water. The resulting suspension is gently neutralized to pH 7 with concentrated HCl (37%). The polymer P separates as a dark red solid, which is collected, and washed several times with cold water/acetone mixtures (1:1 v:v) to remove unreacted monomers and low molecular-weight fractions. After purification, P is dried at 60°C for 3-4 hours. Yield 38 g.

**EXAMPLE 2**

To a suspension of 32 g of finely dispersed 4-{1-[(2,4-dinitrophenyl)-hydrazono]-ethyl}-benzene-1,3-diol in 200 mL of water are added 10 g of phenol and 10 mL of aqueous formaldehyde (40 wt %) at room temperature. To this mixture is added concentrated (37%) HCl (10 mL) with stirring. The resulting dark brown suspension is refluxed four 8 hours at 110 °C to give a dark brown solid. The solid

is filtered, washed several times with cold water and then added to 500 mL of distilled water. The resulting suspension is gently neutralized to pH 7 with an aqueous solution of 1N NaOH. The polymer P separates as a dark red solid, which is collected, and washed several times with cold water/acetone mixtures (1:1 v:v) to remove unreacted monomers and low molecular-weight fractions. After purification P is dried at 60°C for 3-4 hours. Yield 36 g.

EXAMPLE 3

To a solution of 5.0 g of (2,4-dichlorophenyl)hydrazine in 1000 mL of methanol is slowly added 10 mL of concentrated sulphuric acid. After dissolution, a mole equivalent amount of (2,4-dihydroxy)-benzophenone is added at room temperature. After 5 minutes, the solution turns orange and a dark brown solid starts to precipitate. The solid is filtered, washed several times with cold water and then suspended in water. The suspension is gently neutralized to pH 7 with concentrated NaOH. The collected dark brown solid is washed several times with cold water and then added to 500 mL of distilled water. An equivalent amount of 3,5-dimethyl phenol is added and the solution is acidified with 10 mL of HCl (37 %). After complete dissolution, a mole equivalent amount of formaldehyde (40 wt % solution) is slowly added with stirring. The resulting solution is refluxed at 110 °C with stirring. After about 8 hours, P separates as a dark red solid, which is collected, and washed several times with cold water/acetone mixtures (1:1, v:v) to remove unreacted monomers and low molecular-weight fractions. After purification P is dried at 60°C for 3-4 hours. Yield 3.9 g.

Characterisation of a typical sample of polymer P, obtained from 4-{1-[(2,4-dinitrophenyl)-hydrazono]-ethyl}-benzene-1,3-diol, phenol and paraformaldehyde, using elementary analysis, Fourier transformed infrared spectroscopy (FT-IR), ultraviolet-visible spectroscopy (UV-Vis) and <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy.

Element. C, 58.60%; H, 4.24%; N:12.15%. (This analysis nicely fits with a polymer of formula C wherein x = 1 and n= 1 Calcd.: C, 58.67%; H, 4.00%; N:12.44%.)

FT-IR: 3600-3200 (vO-H); 3290 (vN-H); 3100 (v aromaticC-H); 1620 (v C=N); 1615 (v aromaticC=C); 1590 (δ N-H); 1530 (v<sub>s</sub>. NO<sub>2</sub>); 1514 (v<sub>as</sub>. NO<sub>2</sub>); 1330 (δ O-H); 830 (v aromatic C-NO<sub>2</sub>); 710 (δ aromatic C-H ) cm<sup>-1</sup>.

UV-Vis:  $\lambda_{\text{max}} = 390$  nm; shoulder at 420 nm.

<sup>1</sup>H NMR (400.13 MHz, 298 K): (CD<sub>3</sub>COCD<sub>3</sub>): δ = 2.4-2.6 (N=C-CH<sub>3</sub>); 3.7-4.1 (Ar-CH<sub>2</sub>-Ar); 6.4-6.3 (C-H, aromatic); 7.0-6.8 (C-H, phenol ring); 7.6-7.4 (C-H, aromatic); 8.5-8.3 (H, phenol ring); 9.0-8.9 (H, aromatic), 9.1-9.0 (Ar-NH-N), 11.4-11.2 (Ar-OH), 12.0-11.8 (Ar-OH).

5      <sup>13</sup>C NMR: (CD<sub>3</sub>COCD<sub>3</sub>): δ = 40 (Ar-CH<sub>2</sub>-Ar); 102-130 (aromatic); 137 (O<sub>2</sub>N-C aromatic); 143 (HN-C aromatic); 159 (Ar-C=N-); 160-161 (HO-C aromatic) ppm.

The polymer P decomposes before melting at temperatures higher than 300°C.

Two preferred procedures for making the catalysts of the invention are described in Examples 4 and 5.

10      **EXAMPLE 4**

In 100 mL of acetone are dissolved 0.50 g of P and 0.30 g of nickel(II) acetate tetrahydrate (Aldrich) at room temperature. The solution is stirred at room temperature until all acetone is evaporated leaving a reddish residue. This solid, said P-M, is introduced into a quartz reactor which is heated to 800 °C under a

15      protective flow of nitrogen for 2 hours. 0.30 g of a black powdered material is obtained; containing nickel in 7.1 wt. % (ICP-AES analysis).

15      **EXAMPLE 5**

In 100 mL of acetone are dissolved 0.5 g of P, 0.13 g of nickel(II) acetate tetrahydrate (aldrich), 0.08 g of iron(II) acetate tetrahydrate (Aldrich), and 0.08 g of

20      cobalt(II) acetate tetrahydrate (Aldrich) at room temperature. The resulting solution is stirred at room temperature until all acetone is evaporated leaving a violet residue. This crude product, said P-M, is introduced into a quartz reactor which is then heated to 360 °C under a flow of H<sub>2</sub> for two hours. 0.6 g of a black powdered material is obtained, containing iron, cobalt and nickel in a ca. 1:1:1 ratio for an

25      overall metal percentage in the product of 9.2 wt. % (ICP-AES analysis).

A preferred procedure for making a cathode from an HC-P-M material of the invention is described in Example 6.

25      **EXAMPLE 6**

In 100 mL of acetone are dissolved 0.50 g of P and 0.30 g of nickel(II) acetate tetrahydrate (Aldrich) at room temperature. To this mixture, containing said P-M, is

30      added 5.0 g of Vulkan XC-72R (previously activated by heating to 800 °C under N<sub>2</sub> for 2 hours, followed by reflux in aqueous HNO<sub>3</sub> (50%)). The resulting mixture is

stirred at room temperature until all acetone is evaporated leaving a black residue. All acetone is removed at reduced pressure. The solid residue is introduced into a quartz reactor which is heated to 800 °C in a flow of nitrogen for 2 hours.

The solid product is dispersed in a 1:1 (vv) mixture of water/ethanol with stirring.

- 5 To the resulting suspension is added 2.5 g of PTFE (60 wt. % dispersion in water, Aldrich). Vigorous stirring is maintained for ca. 10 min to give a flocculate material.
- 10 The reaction vessel is sonicated until a rubber-like material is formed, which is separated by decantation. This material is rolled on Teflon®-treated carbon paper (Toray) and pressed at 100 Kg/cm<sup>2</sup>. The electrode so formed is baked at 350 °C under a dinitrogen atmosphere.

Two preferred procedures for making an anode of the invention are described in Examples 7 and 8.

#### EXAMPLE 7

- 15 In 100 mL of acetone are dissolved 0.5 g of P, 0.10 g of nickel(II) acetate tetrahydrate (aldrich), 0.065 g of iron(II) acetate tetrahydrate (Aldrich), and 0.065 g of cobalt(II) acetate tetrahydrate (Aldrich) at room temperature. To this mixture, containing said P-M, is added 5 g of Vulkan XC-72R, (previously activated by heating to 800 °C under N<sub>2</sub> for 2 hours, followed by reflux in aqueous HNO<sub>3</sub> (50%)). Acetone is removed at reduced pressure. The solid residue is introduced
- 20 into a quartz reactor which is then heated to 360 °C under a flow of H<sub>2</sub> for 2 hours. The solid product is dispersed in a 1:1 mixture (vv) of water/ethanol with stirring. To the resulting suspension is added 2.5 g of PTFE (60 wt. % dispersion in water, Aldrich). Vigorous stirring is maintained for ca. 10 min to give a flocculate material.
- 25 The reaction vessel is sonicated until a rubber-like, slurry material is formed, which is separated by decantation. This material is pressed at 400 Kg/cm<sup>2</sup> onto a circular steel wire net having a wire thickness of 0.2 mm, a mesh size of 0.2 mm and a radius of 1.75 cm.

#### EXAMPLE 8

- 30 In 100 mL of acetone are dissolved 0.5 g of P, 0.10 g of nickel(II) acetate tetrahydrate (Aldrich), 0.065 g of iron(II) acetate tetrahydrate (Aldrich), and 0.065 g of cobalt(II) acetate tetrahydrate (Aldrich) at room temperature. To this mixture, containing said P-M, is added 5.0 g of Vulkan XC-72R, (previously activated by

heating to 800 °C under N<sub>2</sub> for 2 hours, followed by reflux in aqueous HNO<sub>3</sub> (50%). After stirring for 10 min at 0 °C, 10 mL of an aqueous solution of NaBH<sub>4</sub> (10 wt.%) is added dropwise (CAUTION: the evolved H<sub>2</sub> gas may react with solid catalyst deposited onto the reactor walls). Stirring is maintained for 30 min at room 5 temperature. The solid product is separated by filtration, and washed several times with water/ethanol (1:1, v/v). Then, the solid product is added to a 1:1 (v/v) mixture of water/ethanol with stirring. To the resulting suspension is added 2.5 g of PTFE (60 wt. % dispersion in water, Aldrich). Vigorous stirring is maintained for ca. 10 min to give a flocculate material. The reaction vessel is sonicated until a rubber- 10 like material is formed, which is separated by decantation. This material is pressed at 400 Kg/cm<sup>2</sup> onto a circular steel wire net having a wire thickness of 0.2 mm, a mesh size of 0.2 mm and a radius of 1.75 cm.

#### Electrochemical measurements

Samples of the electrodes according to the invention were prepared as square 15 planar 0.5 cm<sup>2</sup> platelets. Cyclic voltammetry was used to test the anodes towards ferrocene (FcH) oxidation, while the cathodes were tested towards tetracyanoethylene (TCNE) reduction. In both cases were employed CH<sub>2</sub>Cl<sub>2</sub> solutions containing [NBu<sub>4</sub>][PF<sub>6</sub>] (0.2 M) as supporting electrolyte.

Table 1 summarizes the electrochemical results obtained with an anode of the 20 invention, containing Fe-Co-Ni in a 1:1:1 molar ratio, and a cathode of the invention, containing Ni, and also reports comparisons with known electrode materials of common use in fuel cells. The electrochemical data are provided for purely illustrative purposes and do not limit the electrochemical performance of the catalysts of the invention.

25

Table 1. Formal electrode potentials (V, vs. SCE) and peak-to-peak separation (mV) for the one-electron oxidation of FcH and the one-electron reduction of TCNE at different electrode materials (CH<sub>2</sub>Cl<sub>2</sub> solution; [NBu<sub>4</sub>][PF<sub>6</sub>] (0.2 M)).

Electrode	FcH oxidation		TCNE reduction	
	$E^\circ$	$\Delta E_p^a$	$E^\circ$	$\Delta E_p^a$
Fe-Co-Ni-based anode of the invention	+0.41	60		
Anode Pt-Ru <sup>b</sup>	+0.38	180		
Graphite	+0.39	150		
Glassy carbon	+0.42	85		
Ni-based cathode of the invention			+0.21	60
Cathode Pt <sup>c</sup>			+0.21	133
Graphite			+0.22	152
Glassy carbon			+0.23	65

<sup>a</sup> Measured at 0.05 nVs<sup>-1</sup>. <sup>b</sup> From Fuel Cell Scientific <sup>c</sup> From Fuel Cell Scientific

In view of the fact that the electrochemical reversibility of one-electron processes is shown up by a peak-to-peak separation of 59 mV at ambient temperature, it is

5 apparent that the electrodes of the invention behave as effective electron exchangers and, in this sense, are better than the commercial Pt-based electrodes examined.

The electrodes of the invention were tested in typical fuel-cell working conditions, for example 2N H<sub>2</sub>SO<sub>4</sub> and 1N KOH, at 25 °C, CH<sub>3</sub>OH 1M and saturated with air.

10 As shown in Figures 1-4, in either acid or basic solutions, the electrode materials of the invention show high current densities, comparable or even better to/than those of the commercially available materials investigated.

Figures 2 and 3 show the anodic and cathodic polarization curves recorded by single sweep voltammetry for the different anode and cathode materials in 2N 15 H<sub>2</sub>SO<sub>4</sub> solution, respectively.

Comparisons are provided with the corresponding behaviour in deaerated aqueous conditions. The signs of the currents follow the IUPAC convention. Figures 3 and 4 show the pertinent polarization curves recorded in KOH solution.

Electrodes made with the catalysts of the invention, preferentially anodes formed with ternary or binary combinations of Fe, Co and Ni on a conductive support material, and cathodes containing Ni or Co alone on a conductive support material, can be used in single, self-breathing Direct Oxidation Fuel Cells (DOFC), 5 preferentially Direct Alcohol Fuel Cells (DAFC), and more preferentially Direct Methanol Fuel Cells (DMFC), or in Polymer Electrolyte Fuel cells (PEFC) known in the art, showing open circuit voltages (OCV) as high as 1.18 V at ambient temperature (fuelled with H<sub>2</sub>). Appropriate combinations of the metals in the catalyst of the invention can provide a specific power as high as 300 mW/cm<sup>2</sup> at 10 ambient temperature and pressure. The cathodes of the invention are fully tolerant to alcohols, therefore to cross-over alcohols in DAFC's. Commercially available cationic and anionic membranes can equally be used.

As an example, Figure 6 shows the performance of a DMFC formed with electrodes of the invention (Ni-based cathode; Fe-Co-Ni-based anode).

## CLAIMS

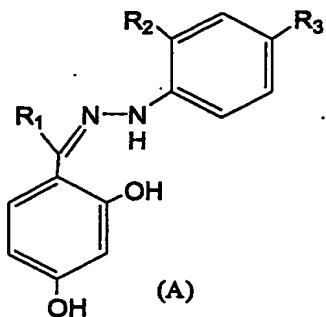
1. Nitrogen-oxygen-carbon polymers obtained by condensation of a 4-{1-[(2,4-di(substituted)-phenyl)-hydrazone]-alkyl}-benzene-1,3-diol with a 3,5-disubstituted phenol and formaldehyde or paraformaldehyde in the presence of either a basic

5 (e. g. NaOH) or acid (e. g. HCl) catalyst in water/alcohol mixtures as solvent and at a temperature comprised between 20-150 °C, and having an average number molecular weight comprised between 1000 and 50000.

2. Polymers according to claim 1 wherein the 4-{1-[(2,4-di(substituted)-phenyl)-hydrazone]-alkyl}-benzene-1,3-diol is a compound of formula

10

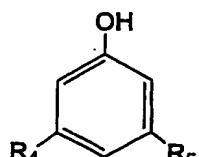
(A):



wherein R<sub>1</sub> is chosen in the group consisting of: hydrogen and a hydrocarbon 15 radical, having from 1 to 10 carbon atoms, possibly halogenated;

R<sub>2</sub> and R<sub>3</sub> each independently represent an electron-withdrawing group selected in the group consisting of hydrogen, halogen, acyl, ester, carboxylic acid, formyl, nitrile, sulphonic acid, linear or branched alkyl or aryl groups, having from 1 to 15 carbon atoms, optionally functionalised with halogens or joined to each other to 20 form one or more condensed cycles with the phenyl ring, and nitro groups.

3. Polymer according to claims 1 and 2 wherein the 3,5-disubstituted phenol is a compound of formula (B):

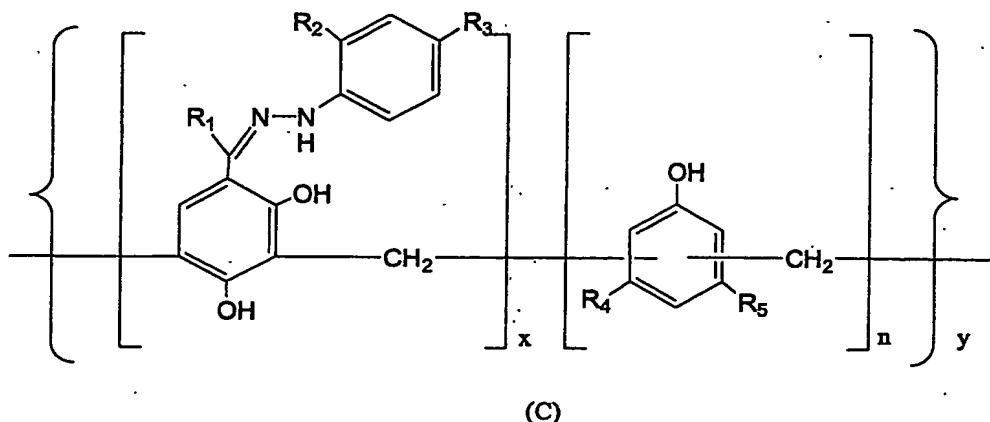


(B)

wherein  $R_4$  and  $R_5$  each independently represent an electron-donating group selected in the group consisting of hydrogen, hydroxyl, ether, amines, aryl and linear and branched alkyl groups, having from 1 to 15 carbon atoms.

4. Polymers according to Claims 1 – 3 having general formula (C)

5



wherein  $y$  can vary from 2 to 120,  $x$  can vary between 1 and 2,  $n$  can vary between 1 and 3 and  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$  and  $R_5$  are as above defined.

10 5. Metal complexes consisting of a polymer according to Claims 1 – 4 and a metal salt.

15 6. Metal complexes according to Claim 5 wherein the metal salt is chosen in the group consisting of iron-, cobalt- and nickel-carboxylates, -halides, -alcoholates, -acetylacetones, -formates, -oxalates, -malonates, and analogous organic salts and mixtures thereof or -carbonates, -oxides and -bicarbonates, and mixtures thereof.

20 7. Complexes according to Claim 6 chosen in the group consisting of: Fe-, Co- and Ni-acetates (and mixture thereof).

8. Catalysts consisting of the complexes according to claims 5 – 7 wherein the metal is reduced either in the solid state with  $H_2$  or in fluid solution systems with appropriate reducing agents.

25 9. Catalysts consisting of the complexes according to claims 5 – 7 wherein the said metal complexes are pyrolysed at a temperature between 500 and 1000 °C, preferentially 800 °C, under inert gas protection (for example  $N_2$ , Ar) for about 2 hours.

10. Electrodes (anodes and cathodes) consisting of the catalysts according to

Claims 8 – 9 and a suitable conductive support.

11. Anodes consisting of the catalysts according to Claims 8 – 9 and comprising binary or ternary combinations of Fe, Co and Ni and a suitable conductive support.

5 12. Cathodes consisting of the catalysts according to Claims 8 – 9 and comprising Ni or Co and a suitable conductive support.

13. A process for preparing a nitrogen-oxygen-carbon polymer according to Claims 1 – 4 wherein said reaction is carried out by condensation of a 4-{1-[(2,4-di(substituted)-phenyl)-hydrazono]-alkyl}-benzene-1,3-diol with a 3,5-disubstituted 10 phenol and formaldehyde or paraformaldehyde in the presence of a basic catalysts.

14. A process according to claim 13 wherein said reaction is carried out in the presence of an acid catalyst.

15. A process according to claims 13 and 14 wherein said reaction is carried out in the temperature range from about 20 to about 150 °C and in the pH range from about 1 to about 14.

16. A process according to claims 13 – 15 wherein said reaction is carried out 20 in either a one-pot or cascade procedure using as separated components a 4-acyl/formyl-benzene-1,3-diol, a 2,4-disubstituted phenylhydrazine, a 3,5-disubstituted phenol and formaldehyde or paraformaldehyde.

17. A process for preparing a complex according to claims 5 – 7 by dissolving a polymer according to Claim 1 – 3 and one or more salts in an appropriate solvent or mixture of solvents, preferentially acetone, in the temperature range from about 20 °C to about 60 °C and submitting the obtained product to reduction..

25 18. A process according to Claim 17 wherein a mixture of metal salts chosen in the group consisting of nickel(II), iron(II) and cobalt(II) salts, alone or in binary or ternary combinations in a preferred stoichiometric ratio is used.

19. A process according to Claim 18 wherein the metal(s) loadings are in the range of about 0.5 % to about 10 % of the total elements plus metal weight.

30 20. A process according to Claims 17 - 19 wherein the reduction step is performed with a flow of H<sub>2</sub> at a temperature between 350 °C and 400 °C for 1-2 hours.

21. A process according to Claims 17 – 19 wherein the reduction step is performed on the complex dispersed in a solvent, with an aqueous solution of hydrazine, or a solution of a tetrahydroborate salt [Y]BH<sub>4</sub>, wherein Y is Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, NR<sub>4</sub><sup>+</sup>, PPN<sup>+</sup> and R<sub>4</sub> is as defined in Claim 3 and PPN<sup>+</sup> is bis(triphenylphosphoranylidene)ammonium, at a temperature between 0 °C and 20 °C for 30 minutes-1 hour.
- 5 22. A process for preparing a catalyst according to Claims 8 – 9 wherein the metal-doped polymers P-M are pyrolysed at temperatures ranging from 500 to 1000 °C under inert gas protection (for example N<sub>2</sub>, Ar) for 1-2 hours.
- 10 23. A process for preparing an electrode according to Claims 10 - 11 in the form of anode for fuel cells, involving mixing together the metal doped polymer materials and either a porous carbon support material or other conductive support materials prior to the reduction treatment according to Claims 20 – 21.
- 15 24. A process according to claim 23 wherein a single metal or a binary or ternary combinations of nickel, iron and cobalt in a preferred stoichiometric ratio, with metal loadings in the range of about 0.5 % to about 10 % of the total elements plus metal weight are used.
- 20 25. A process for preparing an electrode according to Claims 10 and 12 in the form of alcohol-tolerant cathodes for fuel cells, comprising mixing together the metal doped polymer and either a porous carbon support material or other conductive support materials prior to heat-treatment at temperatures ranging from about 500 °C to about 1000 °C under inert gas protection (for example N<sub>2</sub>, Ar) for 1-2 hours.
- 25 26. A process according to Claim 25 wherein the metal doped polymer contains a metal or a mixture of metals with metal loadings in the range of about 0.5 % to about 10 % of the total carbon plus metal weight.
27. Anodes for Direct Oxidation Fuel cells (DOFC) or Direct Alcohol Fuel Cells (DAFC), formed with a catalysed carbon substrate according to Claims 23 - 24 containing metals chosen in the group consisting of iron, cobalt and nickel.
- 30 28. Alcohol-tolerant cathodes for Direct Oxidation Fuel cells (DOFC), or Direct Alcohol Fuel Cells (DAFC), formed with a catalysed carbon substrate according to claims 25 - 26, containing nickel.

29. Anodes for Direct Oxidation Fuel Cells (DOFC) or Direct Alcohol Fuel Cells (DAFC) capable of producing open circuit voltages (OCV) as high as 1.13 V and powers as high as 160 mW/cm<sup>2</sup> at ambient temperature and pressure.
30. Cathodes for Direct Oxidation Fuel Cells (DOFC) or Direct Alcohol Fuel Cells (DAFC) capable of producing open circuit voltages (OCV) as high as 1.13 V and powers as high as 160 mW/cm<sup>2</sup> at ambient temperature and pressure.
31. Anodes for Polymer Electrolyte Fuel cells (PEFC) fuelled with H<sub>2</sub> containing iron, cobalt and nickel in a preferred stoichiometric ratio and overall metal loading between 0.5 and 8 wt %, capable of producing open circuit voltages (OCV) as high as 1.18 V and powers as high as 300 mW/cm<sup>2</sup>.
32. Cathodes for Polymer Electrolyte Fuel cells (PEFC) fuelled with H<sub>2</sub> containing nickel in loadings between 0.5-7 wt %, and capable of producing open circuit voltages (OCV) as high as 1.18 V and powers as high as 300 mW/cm<sup>2</sup>.
33. Fuel cell comprising electrodes according to Claims 10 - 12 and 27 – 32.

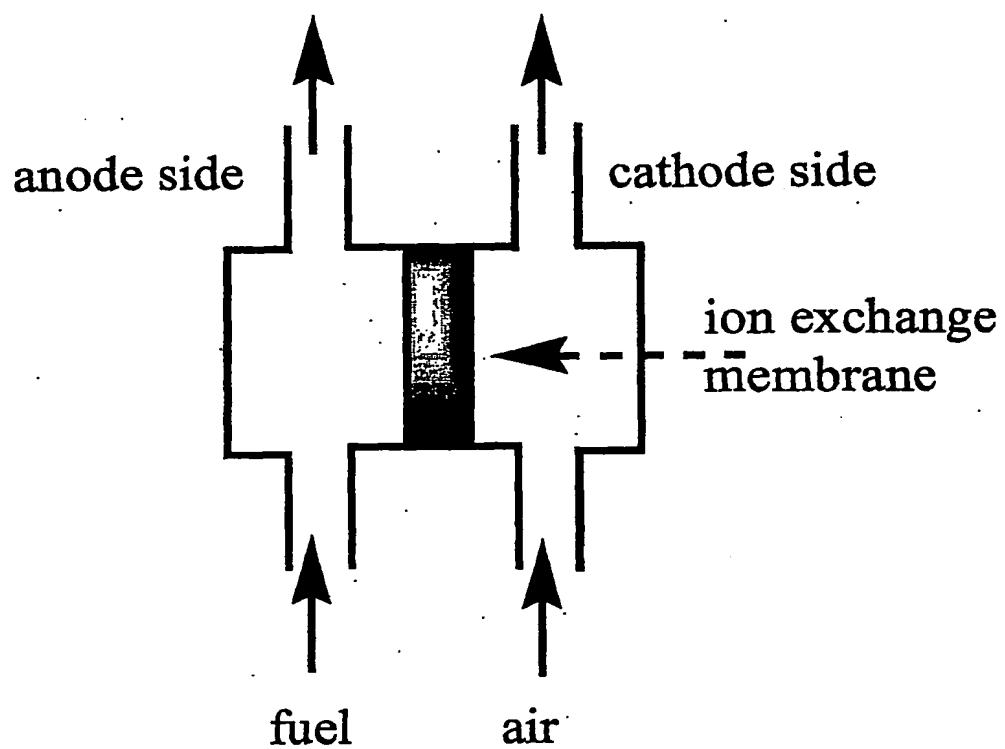


FIG. 1

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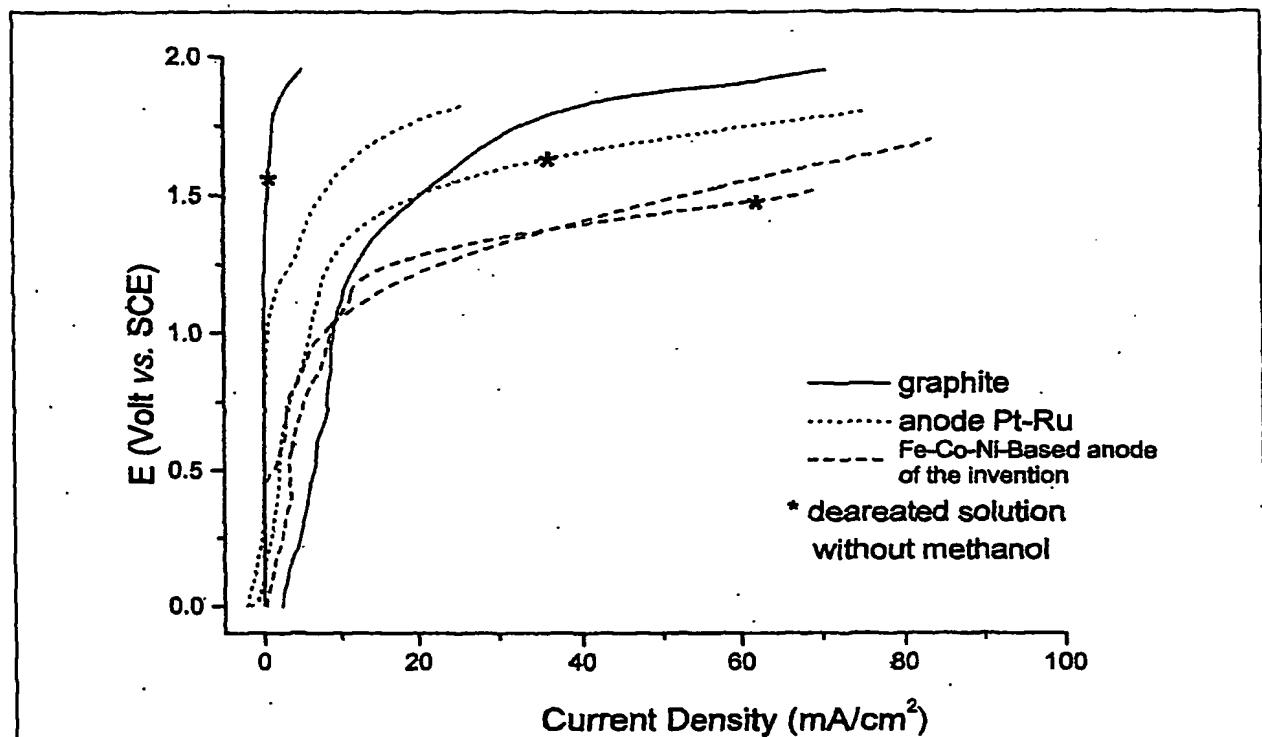


FIG. 2

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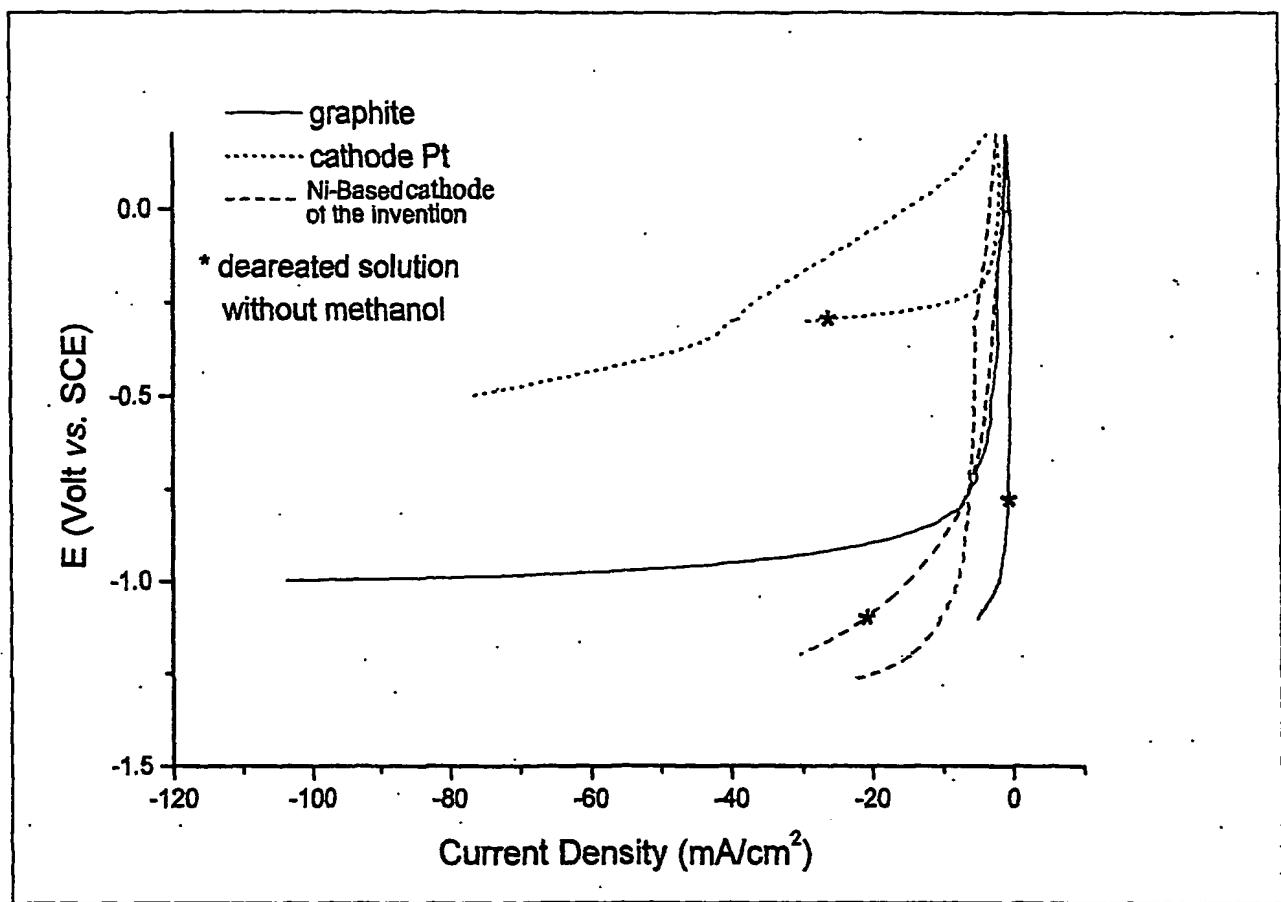


FIG. 3

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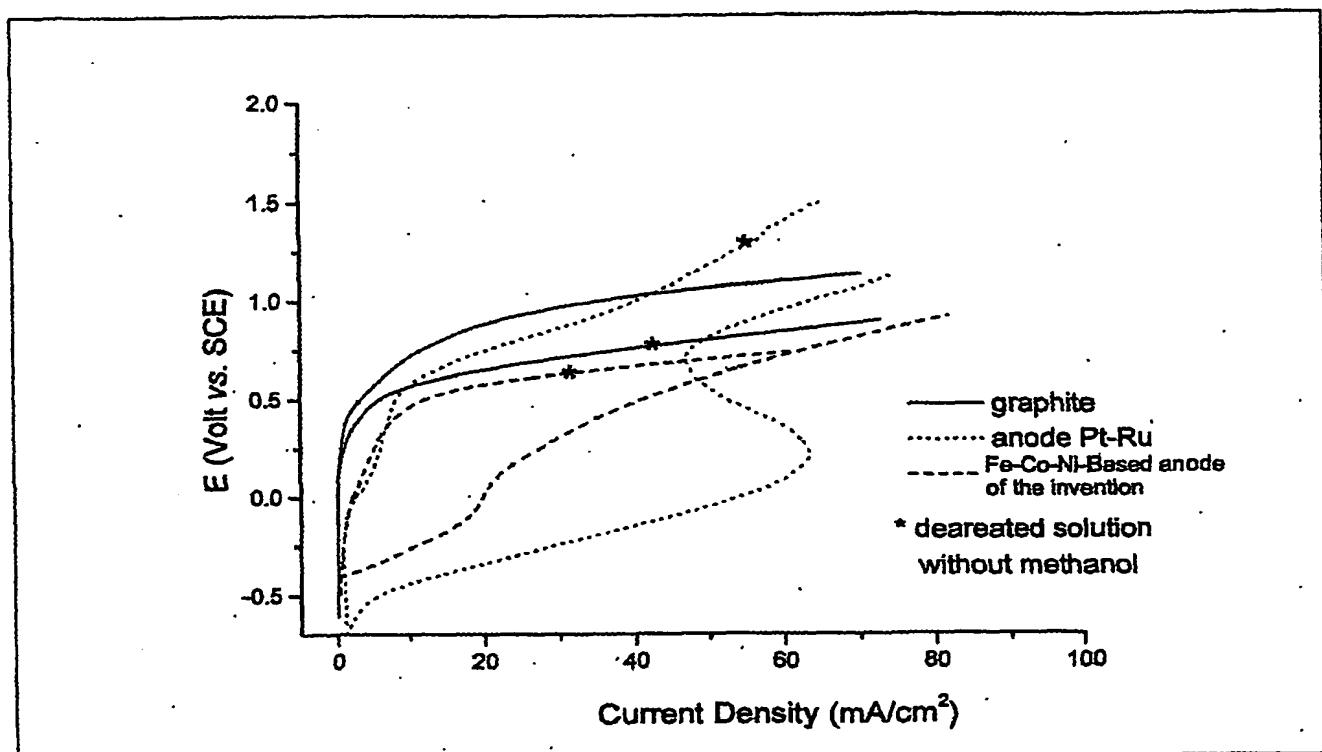


FIG. 4

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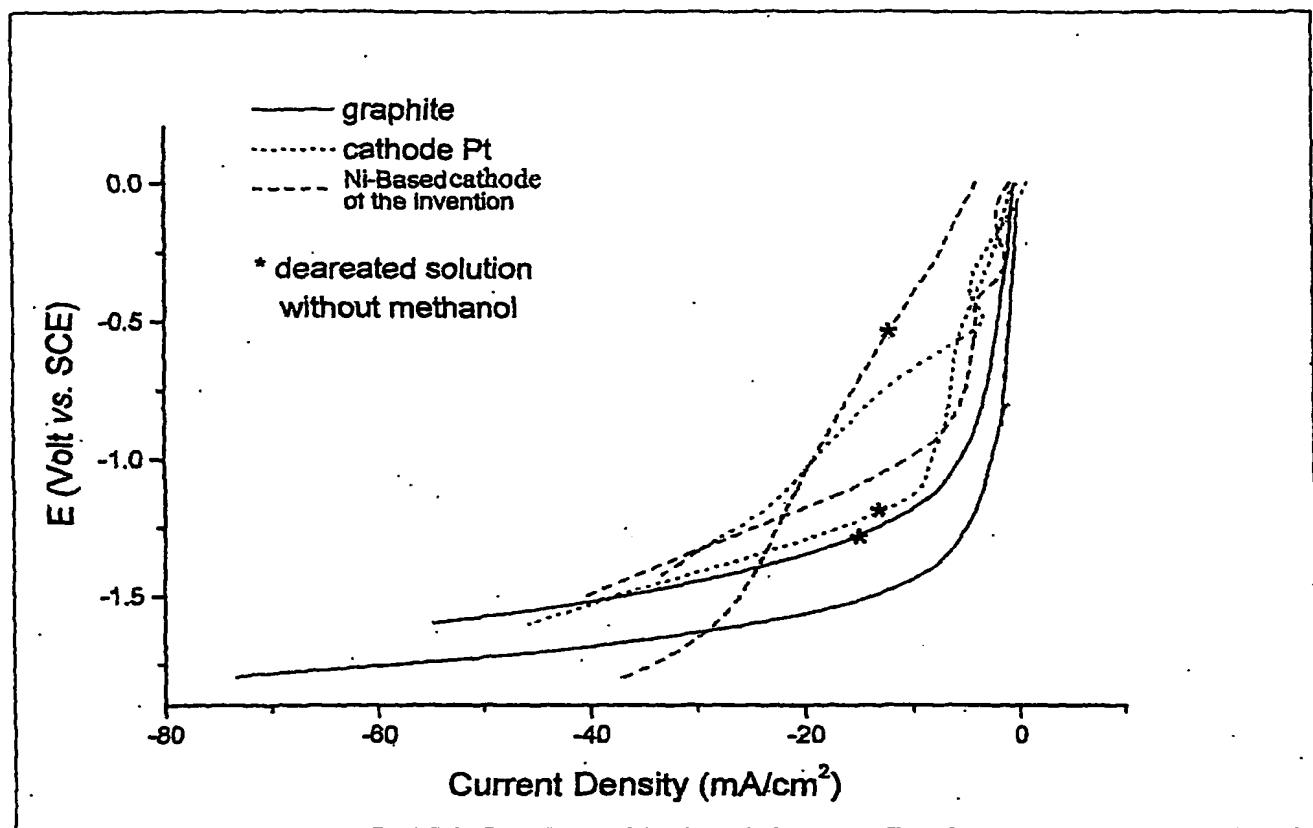


FIG. 5

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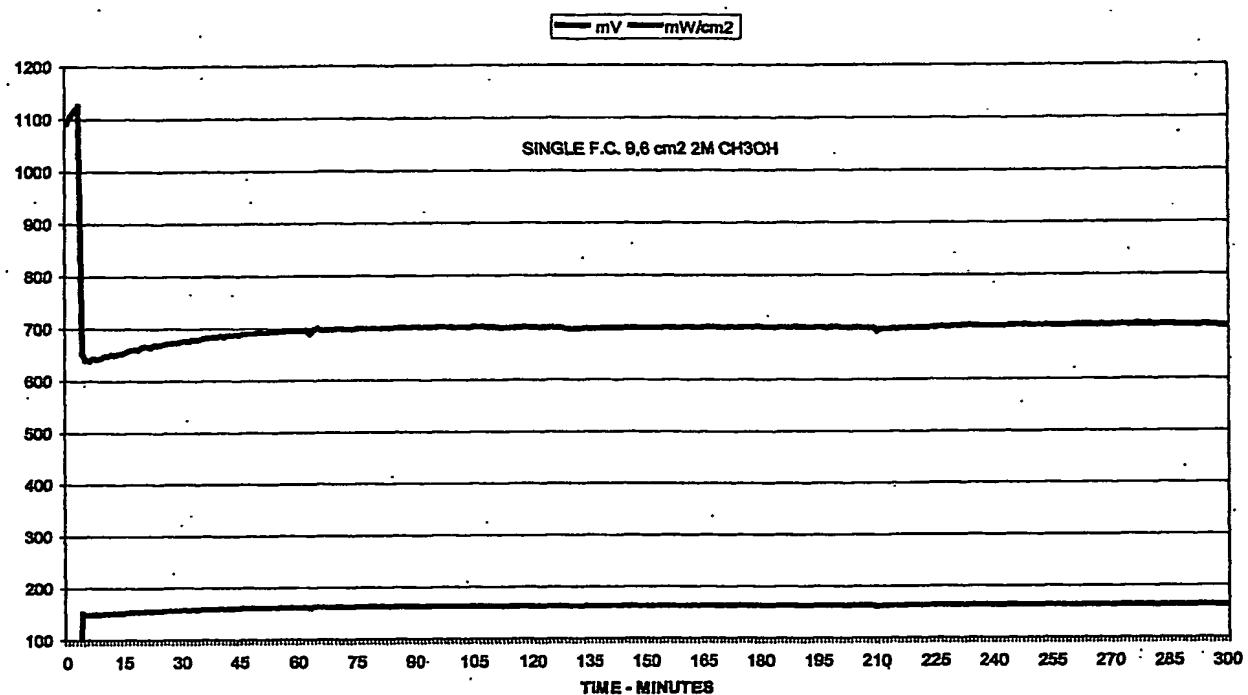


FIG. 6

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International Bureau**



**(43) International Publication Date  
29 April 2004 (29.04.2004)**

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(10) International Publication Number  
**WO 2004/036674 A3**

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C08G 8/08

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**Declaration under Rule 4.17:**

— *of inventorship (Rule 4.17(iv)) for US only*

**Published:**

— with international search report

- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

**(88) Date of publication of the international search report:**  
16 September 2004

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

**(54) Title: PLATINUM-FREE ELECTROCATALYST MATERIALS**

**(57) Abstract:** New metal-based catalyst materials, non-containing platinum, for preferred application to form both alcohol-tolerant cathodes for oxygen reduction and anodes for oxidation of various fuel molecules, and methods of making the said catalysts are provided. Methods for preparing anodes and cathodes for fuel cells are also provided.

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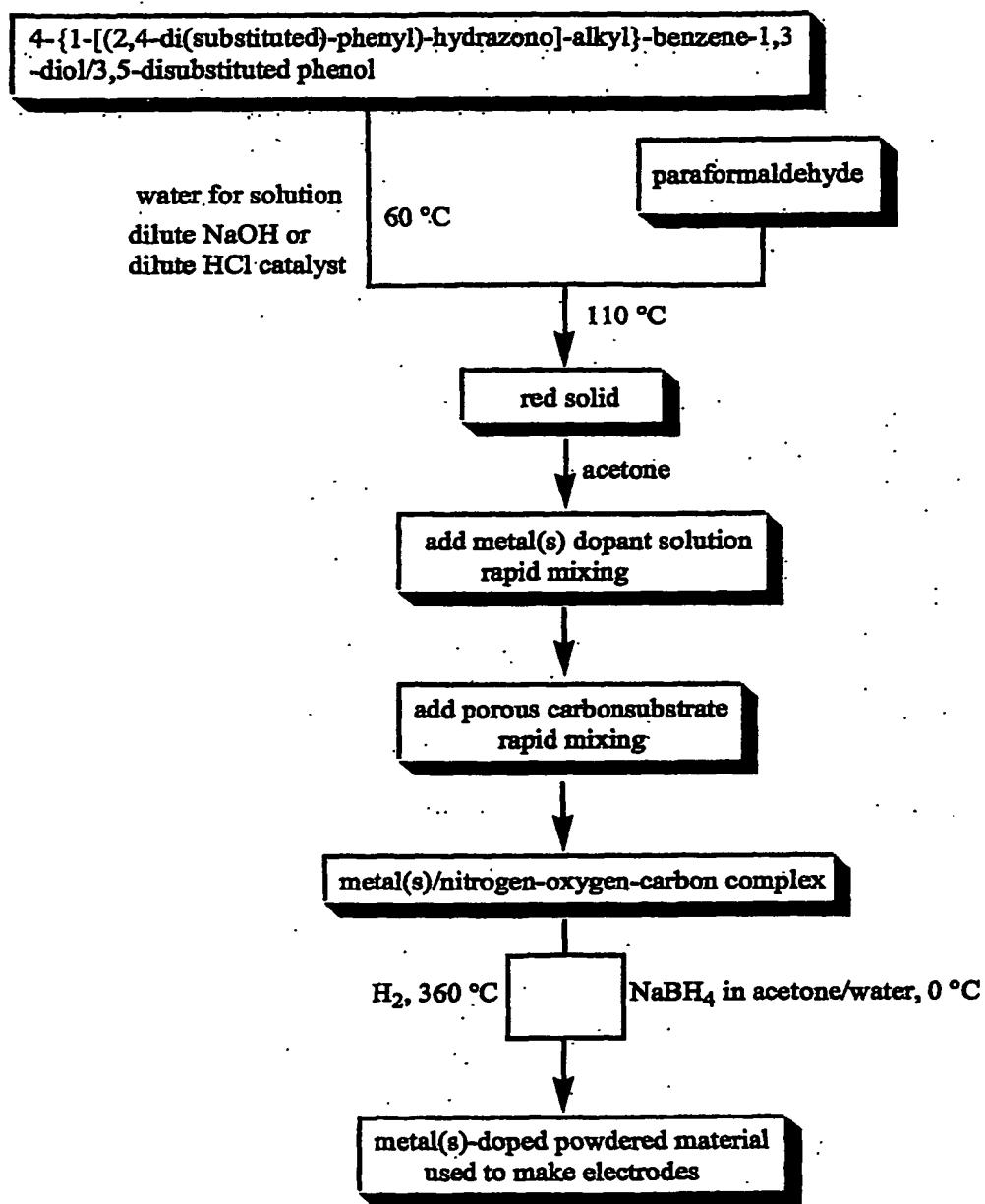


FIG. 7

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/06592

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 7 H01M4/90 C08G8/08

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
 IPC 7 C08G H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, PAJ, WPI Data, EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	LENKA S ET AL: "SYNTHETIC RESINS: XV. CHELATION ION EXCHANGE PROPERTIES OF 2,4-DINITROPHENYLHYDRAZONE OF RESACETOPHENONE-FORMALDEHYDE RESIN" POLYMER INTERNATIONAL, BARKING, GB, vol. 29, no. 2, 1992, pages 103-106, XP008031102 page 103 -page 104	1-7, 13-16
A	---	8-12, 17-22

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

## \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- \*&\* document member of the same patent family

Date of the actual completion of the International search	Date of mailing of the International search report
21 July 2004	29/07/2004

Name and mailing address of the ISA  
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Sánchez García, J. M.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/06592

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	AICH R ET AL: "SYNTHETIC RESINS XXIX: SYNTHESIS AND CHARACTERISATION OF THE RESINS DERIVED FROM 2,4-DINITROPHENYLHYDRAZONE DERIVATIVES OF RESACETOPHENONE-FURFURAL-SUBSTITUTED HYDROXY-AROMATIC COMPOUNDS" POLYMER INTERNATIONAL, BARKING, GB, vol. 34, no. 3, 1994, pages 319-326, XP001191171 page 321 ---	1-22
A	US 4 828 941 A (STERZEL HANS-JOSEF) 9 May 1989 (1989-05-09) cited in the application claims ---	1-33
A	US 5 240 893 A (WITHERSPOON ROME0 R) 31 August 1993 (1993-08-31) cited in the application claims ---	1-33

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/EP 03/06592

**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
  
2.  Claims Nos.: **29–33, partially**  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
  
see FURTHER INFORMATION sheet PCT/ISA/210
  
  
3.  Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

**Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)**

**This International Searching Authority found multiple inventions in this International application, as follows:**

1.  As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2.  As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3.  As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4.  No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

### Remark on Protest

- The additional search fees were accompanied by the applicant's protest.
- No protest accompanied the payment of additional search fees.

**FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210**

Continuation of Box I.2

Claims Nos.: 29-33, partially

Present claims 29-33 relate to an anode/cathode/fuel cell defined by reference to a desirable characteristic or property, namely the Open Circuit Voltage (OCV).

The claims cover all anodes/cathodes/fuel cells having this characteristic or property, whereas the application provides support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT for only a very limited number of such products/compounds/methods/apparatus. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Independent of the above reasoning, the claims also lack clarity (Article 6 PCT). An attempt is made to define the anode/cathode/fuel cell by reference to a result to be achieved. Again, this lack of clarity in the present case is such as to render a meaningful search over the whole of the claimed scope of claims 29-33 impossible. Consequently, the search has been carried out for those parts of the claims 29-33 which appear to be clear, supported and disclosed, namely those parts relating to the anodes/cathodes/fuel cells of claims 29-33 that include the polymers/complexes/catalysts/electrodes according the claims 1-28.

**INTERNATIONAL SEARCH REPORT**

International Application No

PCT/EP 03/06592

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
US 4828941	A	09-05-1989	DE EP JP	3618840 A1 0248394 A2 62296372 A		10-12-1987 09-12-1987 23-12-1987
US 5240893	A	31-08-1993	US	5372981 A		13-12-1994